

***Survey of Recent Developments in the Synthesis,
Structure, and Physical Properties of Nanostructured
Magnetic Materials***

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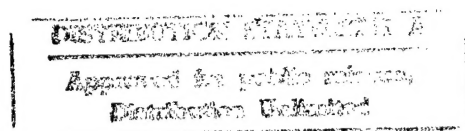
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13. ABSTRACT (Maximum 200 words) Nanocrystalline and nanocomposite materials are polycrystalline materials with grain sizes of up to about 100 nm. This survey reviews the current state-of-the-art in nanoscale design of magnetic materials and identifies new opportunities for future research and applications of these systems. A variety of preparative techniques that lead to magnetic materials with nanometer dimensions are discussed. These techniques include chemical self-assembly processes as well as mechanical fabrication techniques. This is followed by a discussion of the structures, theory and modeling concepts, and novel physical properties with emphasis given to the differences between coarse and fine grained magnetic materials. Finally, there is a discussion of the current and potential applications of nanophase materials that are likely to fuel research into the coming decades.					
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Survey of Recent Developments in the Synthesis, Structure, and Physical Properties of Nanostructured Magnetic Materials

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1. INTRODUCTION

This survey will critically discuss recent advances in the preparation, properties and applications of magnetic materials with nanometer scale dimensions. Nanocrystalline and nanocomposite materials are polycrystalline materials with grain sizes of up to about 100 nm. There are intriguing differences between the behavior of bulk and coarse grained materials when compared to the behavior of particles of those materials that have dimensions closer to the atomic scale. The physical properties of nanocrystalline materials are very often superior to those of conventional polycrystalline coarse-grained materials. Nanoscaled materials often exhibit increased electrical resistivity, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity, and superior magnetic properties in comparison to conventional coarse-grained materials. Particles with nanometer dimensions have been the object of scientific scrutiny for several years because of the unusual electric, optical, and other physical properties that these materials exhibit; however, a clear picture of nanoscaled magnetic materials is beginning to emerge only now. This survey will review the current state-of-the-art in nanoscale design of magnetic materials and identify new opportunities for future research and application of these systems. The various preparative techniques that lead to materials with nanometer dimensions will be presented first followed by a discussion of the structures, theory and modeling concepts, novel physical properties, and applications of nanophase materials that are likely to fuel research into the coming decades.

2. SYNTHESIS

In general, synthetic methods for the fabrication of magnetic materials with nanometer scale dimensions can be classified into two categories: one from molecular precursors (gas condensation, chemical precipitation, aerosol reactions, biological templating, and other self assembly processes), the other from processing of bulk precursors (such as mechanical attrition). Self assembly from molecular precursors is often preferred because it gives better control over a variety of microscopic aspects of the condensed ensemble.

The following is a list of nanostructured magnetic materials and sample materials for the different types that have been synthesized. Since multilayer magnetic materials have been extensively studied in the last several years. They are not included in this survey. This survey is focused on synthetic methods for the preparation of nanoparticles and nanocomposites.

a) Metallic iron, cobalt, nickel, iron alloy and cobalt alloy nanoparticles:

Fe-Pd, Fe-Mg, Fe-B, Fe-C, Co-B, Fe-Co-B, Fe-Cr-B, Co-C

Ag coated Fe, Mg coated Fe

carbon coated alloys: Sm-Co-C, Mn-Al-C

b) Metal oxides: α -Fe₂O₃, γ -Fe₂O₃, Fe₃O₄

c) Ferrites: ZnFe₂O₄, Mg Fe₂O₄, CoFe₂O₄, BaFe₁₂O₁₉

d) Hard magnets: Nd₂Fe₁₄B,

- e) Soft magnets: nanocrystalline $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$.
- f) Quenched ferrofluid and surfactant-vesicle incorporated magnetic particles:
 $\text{Fe}_{1-x}\text{C}_x$ nanoparticle/oleic acid (surfactant)
- g) Multi-property hybrid organic-inorganic nanocomposites:
transparent magnets,
Iron or iron oxide containing nanoparticle-polymer composites:
 Fe_2O_3 /poly(p-ethylphenol), Fe_2O_3 /poly(pyrrole-N-propylsulfonate)
Iron or iron oxide containing nanoparticle- Al_2O_3 or SiO_2 composites.

2.1 Vaporization - condensation process.

One of the earliest methods for producing nanostructured materials was gas condensation from a supersaturated vapor. This method can prepare nanoparticles of elements, alloys, compounds, and mixtures. This technique has a few advantages: it can produce high purity nanoparticles, and it can be used to directly produce films and coatings. Its disadvantage lies in that it is difficult to produce large quantities of nanostructured materials economically, and to produce as large a variety of nanostructured materials as simpler chemical methods can. In order to produce nanoparticles from the vapor it is necessary to achieve supersaturation. The methods for achieving a supersaturated vapor include thermal evaporation, sputtering, electron beam evaporation, or laser ablation. Some of the most recent synthesis studies using vaporization-condensation process are introduced here.

A superparamagnetic nanocomposite of silver and iron oxide has been synthesized by inert gas condensation. The procedure involves 1) coevaporation of silver and iron, 2) in-situ oxidation of iron particles, 3) in-situ compacting of the particles, and 4) post-annealing in an inert or an oxidizing atmosphere. The magnetization plots against H/T falls on a single curve from room temp. to 160 K, providing evidence of superparamagnetism. Annealing treatment modifies the effective magnetic moment size and saturation value of magnetization. The magnetic species has been identified as $\gamma\text{-Fe}_2\text{O}_3$ after the post annealing treatments, while Fe and Fe_3O_4 coexist in the as-prepared loose powder and the as-compacted pellet.^{1,2} High-purity, uniform, and spherically shaped $\gamma\text{-Fe}_4\text{N}$ nanoparticles with high magnetization have been prepared via thermal chemical vapor-phase reaction method, using $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ and NH_3 as starting material³.

Laser vaporization techniques provide some advantages over other heating methods such as the production of high density vapor of metal within an extremely short time (10^{-8}s), and the generation of directional high-speed metal vapor from a metal target for direct deposition of the particles. In laser vaporization, a high energy pulsed laser with an intensity flux of about $10^6\text{-}10^7\text{ W/cm}^2$ is focused on a metal target. The resulting plasma causes highly efficient vaporization so that the local atomic vapor can exceed 10^{18} atom/cm^3 (equivalent to 100 Torr pressure) in the microseconds following the laser pulse. The laser vaporization of metal targets has been combined with controlled condensation in a diffusion cloud chamber to produce metal oxide and metal carbide nanoparticles (10-20 nm) depending upon what reactant gas is present in the chamber.⁴ For the iron oxide nanoparticles, magnetic anisotropy constants have been found to be one order of magnitude

higher than the known bulk values. This technique can also be used to prepare the mixed magnetic nanoparticles of controlled components by sequential or simultaneous vaporization of different metal targets.

2.2 Chemical methods

A variety of chemical methods, such as precipitation, reduction, pyrolysis, aerogel/xerogel processes, and hydrothermal reaction can be used to synthesize nanostructured materials⁵. For example, Amorphous alloy nanoparticles of Fe or Co with B can be prepared by reduction of the iron or cobalt ion in aqueous solution by use of NaBH_4 .⁶ Nanoparticles of amorphous iron carbide can be prepared by thermal decomposition of $\text{Fe}(\text{CO})_5$ in organic solvents containing appropriate surfactant.⁶ The average particle size depends on the type of surfactant used. The nanoparticles of $\alpha\text{-Fe}$, Fe_3C , and Fe_7C_3 can be produced by carbon dioxide laser pyrolysis of vapor mixture of $\text{Fe}(\text{CO})_5\text{-C}_2\text{H}_4$.⁷ The nanoparticles (<35 nm) of $\gamma\text{-Fe}_4\text{N}$ and $\epsilon\text{-Fe}_3\text{N}$ can be prepared by vapor phase pyrolysis of $\text{Fe}(\text{CO})_5\text{-NH}_3$ with a carbon dioxide laser in Ar and N_2 atmosphere.⁸ The manganese zinc ferrite nanoparticles can be synthesized via a hydrothermal reaction.⁹ The pH value of the starting mixture has a decisive influence on the composition of the product, whereas the heating temperature and time determine the size of the particles.

Of the varieties of chemical methods aerosol spray pyrolysis is an attractive technique to produce high purity oxide nanoparticles, such as Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$), gadolinium garnet ($\text{Gd}_3\text{Fe}_5\text{O}_{12}$), manganese ferrite (MnFe_2O_4), and Fe_3O_4 . Aerosol processes in which particles are dispersed in a gas are extensively used to prepare metal oxides, and ceramics in industry. Aerosol spray pyrolysis is a technique in which aqueous metal salts are sprayed as a fine mist, dried and then passed into a hot flow tube where pyrolysis converts the salts to the final products.

Barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) is a new candidate for high density data storage media using perpendicular magnetic recording. It has been found that particle size does not affect the saturation magnetization but does affect the coercivity. When the average particle size decreases, more particles become single domain, which leads to a large coercivity.¹⁰ Therefore, single crystalline nanoparticles of 50 nm and a narrow size distribution are required for this application. Several groups have made efforts to prepare desired barium ferrite nanoparticles. In one preparation¹¹ a homogeneous aqueous solution with the targeted molar ratio of 0.313 BaO -0.215 B_2O_3 -0.100 Na_2O -0.330 Fe_2O_3 was sprayed on the surface of a hot plate at 250 C. The pure and defect-free barium ferrite nanoparticles having average size of 50-70 nm were obtained after crystallization at temperatures below 600C.

In general, aerosol spray pyrolysis involves dissolution of precursor salts, nebulizing the solution, aerosol formation, drying and reacting in a reactor, and particle collection. A wide range of chemical compositions can be created economically using this technique. Most used soluble precursor salts are nitrates that decompose at relatively high temperatures (>600C). However, the decomposition temperature can be lowered by choosing the proper precursors. Recently nanoparticles of $\text{BaFe}_{12}\text{O}_{19}$ (10-20 nm)

have been prepared at a notably low temperature of 425C by using a citrate precursor. The precursor decomposes at 425C to form a metastable spinel-like structure which undergoes time and temperature dependent changes to transform to the final hexagonal structure.¹²

More chemical routes have been designed to produce nanoparticles or nanocomposites. In two most recent synthetic studies, a polymer was used as a matrix for confined synthesis of nanoparticles. In one synthesis study, an α -Fe₂O₃ particle/oligomer hybrid was synthesized by polymerization of iron(III) 3-allylacetylacetonate (IAA) followed by in situ hydrolysis. The polymerization of IAA was dependent upon the temperature and solvent. Crystalline particles from 10-40 nm were finely dispersed in the oligomeric matrix, depending upon the hydrolysis conditions. The nanoparticles below 10 nm were identified to be α -Fe₂O₃ by electron diffraction. The nanosized α -Fe₂O₃/oligomer hybrid showed superparamagnetic behavior.¹³

In another synthetic study, ultrafine (< 150 nm) powders of spinels [MFe₂O₄ where M = Ni(II), Co(II) and Zn(II)], rare-earth orthoferrites [RFeO₃ where R = Sm, Nd and Gd], and rare-earth garnets [R₃Fe₃O₁₂ where R = Sm, Nd and Gd] with good purity and chemical homogeneity were prepared through two new versatile chemical routes. The first route involved the coprecipitation of the desired metal nitrates from their aqueous solution by triethylammonium carbonate solution. (Et₃N, EtOH, H₂O, CO₂ mixtures), in the presence of a water soluble polymer, polyvinyl alcohol (PVA), followed by thermal decomposition. The other process involved complete evaporation of a mixture of optimum amounts of PVA and the desired aqueous metal nitrate solutions, with and without the addition of optimum amounts of urea. The mixture was evaporated to a pasty mass, then heated further to obtain the final spinels and ferrites.¹⁴

In the last a few years, Hendrickson's group has developed a new class of materials, which is high nuclearity, and high spin state Mn-dicarboxylate aggregates, using traditional coordination chemistry synthesis technique.¹⁵ The mixed valence dodecanuclear complex, [Mn₁₂O₁₂(O₂CEt)₁₆(H₂O)₃],¹⁶ is a representative of that class of complexes. This complex has a ground state of 19/2, and exhibits magnetic properties similar to nanoparticles, such as superparamagnetism. These are molecular based magnetic materials, and have a uniform size less than 1.0 nm. After doping into host materials such as polystyrene, the magnetic relaxation properties of the molecules retain. These high spin complexes were synthesized in solution using small polynuclear Mn complexes as a starting material. Other metals such as Fe, and Cu can be inserted into the Mn complexes by reacting the Mn complexes with Fe or Cu containing reagent.

2.3 Water-in-oil microemulsion method

This method was introduced in 1982. The water-in-oil micromulsions, also called reversed micelles have been used to synthesize a variety of nanoparticles of silver halides, superconductors and magnetic materials.¹⁷ Reversed micelles are nanodroplets of water sustained in an organic phase by a surfactant that can hold and dissolve inorganic salts. The inorganic salts are then converted to an insoluble inorganic nanoparticle after chemical reaction and removal of water. For example, superparamagnetic Fe₃O₄ particles (5-20nm)

were prepared by the reaction of $\text{FeCl}_2/\text{FeCl}_3/\text{NaOH}$ within the droplets of water of bis(2-ethylhexyl)sulfosuccinate sodium salt in isooctane solvent.

In a recent synthesis of cobalt ferrite nanoparticles using the reversed micelles method, the size of cobalt ferrite particles from 2 to 5 nm was controlled by the reactant concentration in oil-in-water micelles. Using this method it was possible to obtain the particles either suspended in the solvent to form a ferrofluid or in dry powder. When particles were isolated in a fluid, the interactions between particles were small. The reduced susceptibility increased progressively with the size of the particles and did not reach a plateau. With dry powder made of nanosized particles, the magnetic size was higher. The reduced susceptibility strongly increased with increasing the particle size to reach a plateau for an average size equal to 3 nm. These were explained by the increase in the attractive interactions between particles. By heating the powder, the reduced remanence, M_r/M_s , and the coercivity, H_c , increased with the increase in annealing temperature. This was attributed to the increase in the particle size and to the release of the adsorbed surfactant on the particles. The largest size of particles could be obtained either by annealing of the smallest one or from direct synthesis at room temperature.¹⁸

Another recent sample was the synthesis of the superparamagnetic microspheres of ferrite-polymer composite by incorporating nanometer-sized iron oxide crystals into micron-sized phenolic polymer particles. The synthesis of ferrite particles was conducted in the microenvironment of inverse microemulsions (reversed micelles) and in novel surfactant-based organogels, where interconnecting water channels provided the microenvironment for oxide formation. The microenvironment was used either to restrict oxide growth to the nanometer scale, or to direct growth in specific directions. Subsequently, enzymatic polymerization of p-ethylphenol was conducted in these media to encapsulate the ferrite particles while preserving particle arrangement. The polymer precipitated in spherical morphologies and during precipitation ferrite nanocrystals were incorporated, and uniformly distributed in the polymer matrix.¹⁹

Functionalized reverse micelles were used to prepare Cu and Co nanoparticles differing by their size and shape by reduction of the surfactant metal complexes with N_2H_4 . Fe-Cu alloy (30 at.% Fe) and composite (70 at.% Fe) particles were also prepared. A correlation was shown between the structure of the mesophase in the surfactant system with the size and shape of the formation of pure Cu particles. A functionalized surfactant was used to prepare Co nanoparticles where the size decreased with water content as a consequence of the formation of an oxide shell which prevented the particle growth. Nanopowders of Fe-Cu alloys were formed; magnetization curves before and after annealing were measured revealing a strong correlation with composition which is due to internal structural changes.²⁰

Fe nanoparticles (40-50 nm) coated with Ag have been prepared in two stages. The 1st one consisted of the formation of the magnetic cores in water-in-oil microemulsions. In the second one, silver ions were reduced onto the particles to produce a silver coating.²¹

Nanoparticles of barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) have been synthesized using microemulsion method by different groups. Pillai et al. used water-cetyltrimethylammonium bromide-n-butanol-octane microemulsion system in which the aqueous cores (typically 5-25

nm in size) were used as constrained microreactors for the co-precipitation of precursor carbonates (typically 5-15 nm in size). The carbonates thus formed were separated, dried and calcined to form nanoparticles (<100 nm) of barium ferrite. Nanophase $\text{BaFe}_{12}\text{O}_{19}$ with uniform particle size was synthesized from an alcohol-in-oil microemulsion system where the metal ions were supplied by the surfactant (metal di-2-ethylhexylsulfosuccinate) molecules themselves. A monodisperse, fine-grained precipitate (Ba-Fe oxalate) was ensured by the steric barrier provided by the surfactant monolayer, while the nonaqueous environment promoted stoichiometric co-precipitation. Pure $\text{BaFe}_{12}\text{O}_{19}$ was obtained by calcining the oxalate precursor at or above 950 C.²²

2.4 Matrix-mediated confined synthesis

By matrix-mediated or confined synthesis it is meant that a rigid structure is provided to act as a host or a matrix for the confined growth of the nanoscale magnetic particles. Several such host materials have been explored including those based on carbon fullerenes and nanotubes, organic resins, zeolite and mesoporous solids, and protein cages. The host or matrix not only provides spatially localized sites for nucleation but also imposes an upper limit on the size of the nanoparticles. As a result, this method will produce the nanoparticles with uniform dimensions.

2.4.1 Carbon-arc technique

In the short time since the discovery of spherical²³ and tubular fullerenes,²⁴ much effort has gone into the study of particle confinement within their structures. Carbon-arc techniques are used to synthesize fullerenes and the incorporation of the magnetic species can occur concurrent to this preparation or on subsequent manipulation of fullerene products. In the former method, carbon rods are burned that contain a magnetically active component. The fullerene cage or tube produced will then contain the magnetic species. Guerrer-Piécourt *et al.*²⁵ and others.^{26,27} have reported the routine, direct preparation of magnetically important transition-metals and/or their carbides inside both cages and nanotubes. This route has also been effective in the preparation of carbon-coated magnetic species; researchers here have made a number of finely divided materials including hard magnetic materials such as samarium-cobalt and neodymium-iron-boron alloys.^{28,29} The insertion of magnetic species into fullerenes subsequent to their synthesis has primarily been in the area of nanotubes. Methods have been developed that allow the removal of tube end-caps and the placement of species inside.³⁰ Some metals in the molten state have been placed directly in tubes by capillary action,^{31,32} but the most effective method for magnetic components has been based on solution routes³⁰. Nickel species, for example, have been inserted into tubes via aqueous solutions. Subsequent treatment in oxidizing conditions can produce metal oxides in the tubes, and in some instances on the tube surface as well.³³ Similar chemistry under reducing conditions has resulted in tubes that contain ferromagnetic nickel particles.³⁴ Additionally, techniques have been developed that allow the removal of carbon structures after the formation of the desired nanoscale particle.³³

2.4.2 Ion exchange resins as host structures

Because there can be a large variation in the size of nanotubes and consequently the size of the nanoscale materials grown in them, materials with well-defined, rigid pore structures are also desirable as hosts to nanoparticle growth. Ion exchange resins have rigid pore structures that are a suitable host material. Recently, R.F. Ziolo *et al.*^{35,36} have successfully synthesized nanocrystalline γ -Fe₂O₃/polymer composites using an ion-exchange resin as a host structure. The resin is composed of sulfonated polystyrene, which is cross-linked with divinylbenzene to form a three-dimensional, porous polymer network. During the synthesis, the resin was exchanged with FeCl₂ or FeCl₃ solution, followed by chemical treatment and heating to form the γ -Fe₂O₃/polymer nanocomposite. The nanocomposite is an optically transparent magnetic material.

2.4.3 Microporous or mesoporous materials as host structures

Microporous solids such as zeolites and mesoporous solids have rigid pore structures as well. Though the use of these materials for the growth of semiconductor nanoparticles (quantum particles) is known,³⁷ the growth of magnetic particles in these systems has been much less studied and, interestingly, often motivated by particle properties other than magnetism (*e.g.*, catalytic activity). Of the reported investigations, most have concentrated on the use of zeolite hosts; some researchers for example have examined the preparation of iron³⁸ and cobalt³⁹ metal and iron oxide,⁴⁰ while others have looked at ferromagnetic alkali-metal clusters in various zeolites. Very few reports have extended to the study of mesoporous materials. One of the few examples found that iron oxide particles can be readily prepared in the silicate, MCM-41.⁴¹ MCM-41 is a new family of molecular sieves, and possesses a regular hexagonal array of uniform pore opening. The pore size is in the range 2-10 nm. It has been found that the nanoparticles of Fe₂O₃ encapsulated into the uniform pores of MCM-41 have a uniform size of about 4 nm, and the bandgap of the resulting Fe₂O₃ particles is widened from 2.1 to 4.1 eV. The magnetic properties of this system remain undetermined.

A typical preparation of magnetic nanoparticles using zeolite as a host structure can be illustrated with the synthesis of iron clusters embedded in the Faujasite-type zeolite NaX.⁴² The crystal structure of NaX consists of SiO₄⁻ and AlO₄⁻ tetrahedra forming cubooctahedra, which are interconnected via six-membered rings. The overall frame contains supercages which provide enough space to host molecular units of sizable dimensions (<1.3 nm). The NaX solids are saturated with Fe(CO)₅, and followed by thermal decomposition. The size of iron nanoparticles depends upon the condition of thermal decomposition of the system Fe(CO)₅/NaX. Thermal decomposition under continuous vacuum up to 453 K leads to iron particles larger than 10 nm, whereas thermal decomposition up to 723 K under argon atmosphere leads to clusters in the 3-4 nm range, and in contrast clusters in the 2 nm range could be obtained by thermal decomposition up to 453 K under static vacuum and subsequent heating up to 823 K under continuous vacuum.

2.4.4 Biomolecules as host structures

A class of proteins known as the ferritins provides nature with a method of synthesizing nanoparticles of iron oxyhydroxides and oxyphosphates. The ferritins operate as iron storage, iron transport, and iron-detoxification proteins. A ferritin molecule consists of 24 subunits that self assemble to form a spherical cage with an external diameter of about 12 nm and an internal cavity diameter of about 8 nm. The assembled structure has channels that connect the internal cavity with the external space so that the ions can diffuse into or out the cavity. The empty protein cage is known as apoferritin. The iron oxyhydroxide or phosphate cores of ferritins can be easily removed leaving the apoferritins which can be used as reactors for the synthesis of magnetic nanoparticles. This method has been used to build ferrimagnetic iron oxides and other oxide cores in the supermolecular protein cages. In addition, the iron oxyhydroxide cores of ferritin can be modified in vitro to produce new structures and phases. Although the current research in this respect is focused on making three-dimensional superlattices of nanoscale structures for optoelectronic applications. This method has a potential in making new magnetic nanostructured materials that are important in science and technology.^{43,44}

All of these materials, those based on fullerenes as well as microporous and mesoporous solids, offer a controlled method for the synthesis of magnetic nanoparticles of specific size. Particularly significant are the ion exchange resin, the zeolitic and mesoporous hosts because of their ability to consistently produce particles of uniform dimensions, potentially up to several tens-of-nanometers in diameter, and because most investigations with these hosts have not been geared specifically toward the production of magnetic compounds. Further investigation into these systems is needed to fully explore their utility for the routine preparation of magnetically important materials. Once this chemistry is established, then the development of technologies based on nanoscale magnetic particles can quickly follow.

2.5 Mechanical attrition

Mechanical attrition or mechanical alloying is a versatile process to prepare nanostructured materials in large quantities. This technique has been developed as an industrial process to prepare alloys and composites that can not be synthesized via conventional casting process, *e.g.*, uniform dispersions of ceramic particles in a metallic matrix. Mechanical attrition is a non-equilibrium process which has produced a broad range of alloys, intermetallics, and composites in the amorphous and nanocrystalline state. Recently, efforts have been made to apply this technique to prepare nanostructured permanent magnets with high performance.

A most recent effort was to apply this method to prepare hard magnets $\text{Sm}_2\text{Fe}_{17}$ and $\text{Nd}(\text{Fe},\text{V})_{12}$ nitride and carbide. Starting from the elemental metallic powders, ball milling produced either a two-phase material of $\alpha\text{-Fe}$ and amorphous Sm-Fe or an intimate mixture of the elements, if Nd was the rare earth metal involved in the processing. The intermetallic phases were formed by solid-state reaction at relatively low temperatures (about 700 C) leading to a nanocrystal microstructure. A solid-gas reaction in N_2 or C_2H_2 atmospheres at 450-500 C was used to introduce nitrogen or carbon atoms. Optimum parameters resulted

in a coercivity of up to 32 kOe for the 2:17 nitride and 23 kOe for the 2:17 carbide. Remanence and energy product of these magnetically isotropic materials were equivalent to similarly prepared Nd-Fe-B samples, but their properties at elevated temperatures were superior because of the high Curie temperature and the large anisotropy field. Zn-bonded $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ samples reached coercivities of more than 40 kOe. Crystalline $\text{NdFe}_{11}\text{Ti}$ samples with the 1:12 structure showed partial amorphization upon nitrogenation.⁴⁵

In another synthesis study, a group from Japan applied mechanical alloying to prepare a new class of permanent magnets called exchange spring magnets that consisted of exchange coupled hard and soft magnetic phases at the nanometer scale. Such an exchange coupling helps these magnets to exhibit high coercive force as well as high saturation magnetization, resulting in a higher energy product. A recent surge in research interest in this field showed the nitride of rare earth-iron compound to exhibit good magnetic properties. Also, the application of mechanical alloying technique for the synthesis of the rare earth-iron compound was more versatile. In their synthesis, $\text{Sm}_x\text{Fe}_{100-x}$ ($x = 7, 9, 11, 13$) was mechanical alloyed. In the as milled condition, α -Fe was found to coexist with an amorphous phase. Heat treating the mechanical alloyed powder gave the $\text{Sm}_2\text{Fe}_{17}$ compound (hard phase) and α -Fe (soft phase). The formation of the hard phase as a function of Sm content and heat treatment temperature was studied. The heat treated samples were nitrated for different duration and at various temperatures. Good magnetic properties were observed for alloys with 9 at.% Sm. Improvements in the magnetic properties and thermal stability of the hard phase was studied by the substitution of Co, Cr and Si for Fe. Co substitution for Fe increases both the remanence and the coercivity, resulting in a higher energy product.⁴⁶

2.6 Electrodeposition

Electrodeposition has mainly been used to prepare nano-processed soft magnetic materials such as pure nickel and cobalt as well as binary nickel-iron and ternary nickel-iron-chromium alloys.⁴⁷ Nanoprocessing can be considered a distinct form of grain boundary engineering by which property enhancements are achieved by deliberately increasing the volume fraction of grain boundaries and triple junction. The bulk materials or thin films nanoprocessed by electrodeposition have a grain size in the nanometer scale that are also called nanocrystalline materials.⁴⁸

Nano-processing by electrodeposition improves the overall performance characteristic of soft magnetic materials used in recording head application.⁴⁹ Permalloy containing 15-25 Fe and 0.05 wt.% Cr that has been nano-processed by electrodeposition using a metal chloride solution at 23C and 0.05A/cm² has a grain size of the electrodeposits of 7-16 nm and enhanced properties such as coercivity, electric resistivity, hardness, and corrosion behavior for recording head applications.⁵⁰

3. STRUCTURE-PROPERTY OVERVIEW

Because of the extremely small dimensions of nanophase materials, a large volume fraction

of the atoms is located at the grain boundaries and surfaces. Nanostructured materials thus represent a special state of solid matter that consists primarily of incoherent interfaces (grain or interphase boundaries) formed between nanometer-sized crystallites of different crystallographic orientations. The atomic arrangement in the incoherent interfaces is characterized by a reduced density and nearest neighbor coordination number relative to the glassy or crystalline state. The reduced density and coordination is due to the misfit between the crystallites of different crystallographic orientations that are joined together at the interfaces. The reduced density and nearest neighbor coordination number leads to a new type of atomic structure which exhibits properties that differ (sometimes by many orders of magnitude) from the ones of crystals and glasses with the same chemical composition.⁵¹ Nanostructured alloys permit the alloying of components that are immiscible in the crystalline and/or glassy states. New concepts of nanocomposites and nanoglasses are being intensively investigated. Although discovered less than 15 years ago, nanostructured materials have started to enter the regime of technology applications. There is a great potential for applications of the nanoscaled materials in the future. The extensive investigations in recent years on structure-property correlations in nanocrystalline materials have begun to unravel the complexities of these materials, and pave the way for successful exploitation of the nanoscaled design principles to synthesize better materials than hitherto available.

When materials possessing long-range magnetic order such as ferromagnetism and antiferromagnetism are reduced in size, the magnetic order can be replaced by some other magnetic states. One way to reduce the dimension of the ordered magnetic regions is to isolate them inside non-magnetic matrices by precipitation from solid solution. Another way is to form a composite of nanometer-sized magnetic and non-magnetic species. For these nanocomposites their magnetic behavior becomes either paramagnetic or superparamagnetic.⁵² Because of the ease in control of the magnetic behavior that results from control of the processing parameters, such materials present great possibilities for the atomic engineering of materials with specific magnetic properties.

3.1 Quantum Tunneling

Quantum tunneling effects have been recently reported in several nanostructured materials.⁵³⁻⁵⁶ These observations are possible partly because of significant advances both in the ability to obtain magnetic systems of almost any desirable size, shape and composition, and in the instrumentation development for detection of extremely weak magnetic signals. The observation of steps at regular intervals of magnetic field in hysteresis loops was interpreted as evidence for thermally assisted, field tuned resonant tunneling between quantum spin states in a large number of identical high spin molecules. The study of low temperature magnetic relaxation in nanostructured materials has provided the opportunity to observe the occurrence of quantum tunneling of magnetization. As the magnetization is a classical vector, this effect is also referred to as macroscopic quantum tunneling.

Clusters of metal ions are a class of compounds actively investigated for their magnetic properties, which changes from those of simple paramagnets to those of bulk magnets. In addition to the coexistence of classical and quantum behavior, these systems

may help find the link between simple paramagnetism and bulk magnetic behavior.⁵⁷

3.2 Anisotropy

The most common types of anisotropy are crystalline anisotropy, shape anisotropy and exchange anisotropy, of which crystalline anisotropy and shape anisotropy are most important in nanostructured materials. Magneto-crystalline anisotropy arises from spin-orbit coupling and energetically favors alignment of the magnetization along a specific crystallographic direction. Shape anisotropy is the result of departure from sphericity of magnetic particles and is predicted to produce the largest coercivity. El-Shall *et al.* have found that, for the iron oxide nanoparticles, magnetic anisotropy constants were one order of magnitude higher than the known bulk values.⁴ The magnetic property study of the nanocomposites of silver and iron oxide synthesized by sputtering, gas condensation and *in-situ* oxidation indicated that these composites were superparamagnetic above ~100 K.^{58,59} At lower temperatures, hysteresis measurement provides evidence for the occurrence of an unidirectional anisotropy, which is considered to be caused by interactions between the magnetic phases coexisting in the composites.⁶⁰

An induced magnetic anisotropy was found to increase with the field annealing time in nanocrystalline Fe-Cu-Nb-Si-B alloys. A high relative initial permeability, a flat B-H loop, and low remanence were obtained by transverse field annealing for a short time.⁶¹

3.3 Analytical Instrumentations

Typical instruments used in analyzing magnetic nanostructured materials include transmission electron microscopy, scanning electron microscopy, spin polarized scanning tunneling microscopy, x-ray diffraction, atomic force microscopy, magnetic force microscopy, magneto-optical Kerr rotation, nuclear magnetic resonance, electron spin resonance, Raman spectroscopy and IR spectroscopy, low energy electron diffraction, electron energy loss spectroscopy and spin polarized photoemission studies.

A new design for a Moessbauer *in situ* cell for the studies of catalysts and nanometer-sized particles has been reported.⁶²

4. THEORY AND MODELING

4.1 Single Domain Particles

Magnetic particles of nanometer sizes are mostly single domain as the formation of domain walls becomes energetically unfavorable.⁶³ As the particle size further decreases below the single domain value, the magnetic moment of the particles will be gradually affected by thermal fluctuation and they behave paramagnetically with giant moments. This superparamagnetism exhibits zero coercivity, but will cease to exist below the blocking temperature at which thermal energy is not sufficient for the moment to relax during the time of the measurement. Stoner-Wohlfarth theory was developed to describe the behavior of an assembly of single-domain particles.⁶⁴ A more recent theory by Holz and Scherer address the coupling between magnetic particles in nanostructured materials⁶⁵. The issue of

exchange coupling between magnetic nanoparticles has drawn much attention in recent years as it will have significant impact on both the understanding and application aspects of nanostructured magnetic materials.

4.2 Modeling

Combining the classic micromagnetic theory with the Landau-Lifshitz-Gilbert gyromagnetic equations, recent modeling studies have led to much improved understanding of fundamental magnetization processes in magnetic thin films. Hysteresis properties and transition noise behavior of longitudinal thin film recording media with advanced microstructures has been studied via micromagnetic modeling. The modeled nanocrystalline thin film consists of grains with nanocrystalline subgrain-structures: each normal magnetic grain contains seven subgrains and the subgrains form bicrystal structure within a normal grain. High coercive squarenesses can be achieved for films with a weak exchange coupling through the normal boundary. If the inter-subgrain exchange coupling is kept small, transition noise can be very low and the effective width of zigzags in a transition is essentially determined by the size of a subgrain. The high coercive squareness and extremely low noise make the nanocrystalline films suitable for ultra-high density recording applications.⁶⁶ Chui and Tian have recently studied the finite temperature magnetization reversal of single domain nanostructures (particles and wires) of different materials with Monte Carlo and analytic techniques. For large structure diameters, there are different reversal mechanisms at different orientations of the external field. For small structure diameters, growth usually starts with the nucleation and a subsequent depinning of domain walls at the end(s) of the structure. The nucleation energy of the domain wall in a magnetic field approaches zero near the coherent rotation limit at small aspect ratios and at fields less than the coherent rotation limit at large aspect ratios. As the domain wall energy approaches zero the domain wall width can remain finite. For small diameters there is a significant temperature dependence in the coercive field.⁶⁷

5. APPLICATIONS

Magnetic materials of nanoscale have found increasing applications that are important to our nation's defense needs. Compact but strong magnets that are made of nanocomposite of soft and hard magnetic materials can be manufactured with desirable coercivity and remanence to suit to various field applications. Soft ferrites of nanoscale exhibit enhanced electromagnetic wave absorbing characteristics that may find important application in object shielding. They also have potential to be used as advanced noise filters. New applications of ferrites such as ferrite carriers and toners for electrophotocopy and biochemical applications is expanding. Typical applications of those exhibiting desirable magnetoresistive properties include magnetic filed probes, magnetic read head, contactless switches, position sensors in brushless motors, which may eliminate contact noise - a significant noise contribution in electronic devices, and pattern recognition, in which a magnetically printed pattern is scanned using a highly sensitive magnetic sensor. Magnetoresistive-random-access-memory

(MRAM) are currently being developed utilizing the giant magnetoresistance technology. Rewritable magneto-optical recording materials of nano-crystal sizes possess improved signal-to-noise ratio as compared to their large grain counterparts, which lay the foundation for the future development of high density short wavelength magneto-optical recording materials. Grain size of the order of a few nm is also essential for the development of ultra-high density magnetic recording medium (beyond 5-10 Gbit/in²). Optically transparent nanocrystalline magnetic switching technologies. Applications of ferrofluids include lubrication, sealing, air-moisture absorption, shock absorption and electrically conducting fluids for electromechanical systems. The possibility of intensifying convection at the expanse of a magnetic field converts a magnetic fluid into a highly effective and controllable heat carrier. Ferrofluids also find device application such as sensors and actuators and are used as magnetic toner in xerography and as contrast agent in magnetic resonance imaging. Nanoscaled magnetic materials may have significant impact in the field of biology and medicine, the details of which are outlined in the following section.

5.1 Magneto-optical Recording

High density rewritable magneto-optical Kerr effect recording is now a reality. Future development includes application of shorter wavelength diode laser for higher recording density and preparation of films with sufficiently small grain size for the reduction of media noise. Studies have found that nanoscaled transition metal multilayers, in particular Co/Pt multilayers, compare favorably with amorphous rare earth-transition metal alloys GdTbFe at short wavelengths. The Co/Pt multilayers have a Kerr rotation which is larger by about a factor of 3 in comparison to GdTbFe in the 400 nm region.⁶⁸ One of the deficiencies of the Co/Pt multilayers is that they are polycrystalline rather than amorphous although their grain size is quite small.

MnBi-based compounds have rather large Kerr rotation relative to the amorphous alloys and Co/Pt multilayers. But the polycrystalline nature of the material plus its relatively large grain size makes it unsuitable for practical recording film due to high media noise. It has also a structure instability near its Curie temperature, which causes difficulties in the writing process. Recently, it has been reported⁶⁹ that Al doping increased MnBi's Kerr rotation, reduced the grain size and improved the thermal stability. However, Sellmyer *et al.* have found that Al doping does not enhance the Kerr rotation nor eliminate the high temperature structural stability. It does promote small grain sizes which are required for a low noise recording medium.⁷⁰

Both MnBi-based compounds and garnets are polycrystalline materials exhibiting large Kerr rotations at blue wavelength. They possess high potential as practical recording media. Synthesis of nanocrystalline materials with grain sizes less than 30 nm is desirable for low media noise.

5.2 Magnetic Sensor

Typical applications include: magnetic field probes; magnetic read head; contactless switches; position sensors in brushless motors, which may eliminate contact noise, a significant noise contribution in electronic devices; pattern recognition, in which a

magnetically printed pattern is scanned using a highly sensitive magnetic sensor made of giant magnetoresistance (GMR) materials. Bridge magnetic sensors made of GMR materials offer signals that are 3-20 times as large as those of a traditional magnetoresistive sensor. They are linear over most of their operating range and exhibit superior temperature stability.⁷¹

Most of the studies on GMR materials involve metal-metal systems in which magnetic metal particles are dispersed in non-magnetic metal matrix, or magnetic metal layers are separated by non-magnetic metallic spacers. Recently, large magnetoresistance has been observed in metal-insulator-metal trilayers, where two magnetic layers are spaced by a thin insulator film.^{72,73} The results seem to support the claim that large magnetoresistance is due to the spin polarized tunneling of electrons between two magnetic metals through a thin Al_2O_3 insulator. These findings have attracted much attention because of the interesting problem of "Spin Tunneling" that is involved in such systems. GMR in granular materials using insulating matrix has also been reported recently.⁷⁴

5.3 High Density Magnetic Memory

The areal density in longitudinal magnetic recording has surpassed the 1 Gbit/in². Level and continues to grow at a 30-60% compound rate per year.⁷⁵ It is anticipated that 10 Gbit/in². densities can be achieved by the turn of the century by extending the current technology using scaling laws.⁷⁶ A further increase will require major improvements in head, media and channel technologies.⁷⁷ Of particular interest are low noise high coercivity media. Currently, CoPtCr based continuous media are used. These consist of exchange coupled grains with sizes of the order of several 10 nm. A reduction of the grain size and control of the intergrain exchange coupling would be highly desirable for further noise reduction, which is required in ultrahigh density, beyond 5-10 Gbit/sq.in. media. Reduction of grain size, however, will eventually lead to superparamagnetic particles, unsuitable for recording. Such limitations can be overcome by the design of novel nanocomposite materials with larger intrinsic magnetic anisotropies.^{78,79} An especially interesting approach is the fabrication of completely exchange decoupled magnetic nanoparticles which would constitute media in which the transition between adjacent bits is controlled by the physical location of the particle, rather than by the demagnetization zone in a continuous media. This could eliminate the transition noise altogether, if one succeeded in developing a process to fabricate regular arrays of such particles.⁸⁰ Such processes could include nanolithography, as suggested by Chou *et al.*^{81,82} They have prepared patterned media using an injection molding process for patterning and subsequent electrodeposition of Ni. Isolated and interactive arrays of magnetic Ni pillars were fabricated. Unique magnetic properties were obtained by controlling size, aspect ratio and spacing of the pillar array. Particles as small as 15 nm in diameter have been reported and nominal areal densities of order 250 Gbit/sq.in. were suggested. Addressability (write, read, data rate etc.) remains an open issue.

Ni-Al nitride nanocomposite was shown to have potential applications as high density recording media, as are other finely divided dispersions of ferromagnetic metals in insulating matrixes⁸³. The Ni-Al nitride nanocomposite shows a moderate coercive field of

35 Oe at 300 K and, in common with ultrafine particles of ferromagnetic materials, shows superparamagnetic behavior.

Magnetoresistive random-access-memory (MRAM), an integrated magnetic memory technology that uses magnetic storage and magnetoresistive reading with semiconductor support circuits⁸⁴ are currently being developed using GMR materials.

5.4 Optically Transparent Materials

A magnetic material with appreciable optical transmission in the visible region at room temperature has been found in a γ -Fe₂O₃/polymer nanocomposite. Optical studies show that the small particle form of γ -Fe₂O₃ is considerably more transparent to visible light than the single crystal form. The magnetization of the nanocomposite is greater by more than an order of magnitude than those of the strongest room temperature transparent magnets, FeBO₃ and FeF₃.³⁵

Real time transitions from metallic (YH₂ or LaH₂) to semiconducting (YH₃ or LaH₃) behavior was recently found to occur in the coated films during continuous absorption of hydrogen, which was accompanied by pronounced changes in their optical properties, for example, it changes from a shiny mirror to a yellow, transparent window.⁸⁵ Although the time scale on which this transition occurs is at present rather slow, there appears to be considerable scope for improvement through the choice of rare earth elements and by adopting electrochemical means for driving the transition. This switchable optical property may find important technological applications.

5.5 Soft Ferrites

Ferrites offer many advantages in rf applications where the complex permeability can be modified by an external field or by changes in composition. The complex permeability of the ferrite of YIG family was measured as a function of magnetic field to characterize the control of the permeability at various temperatures.⁸⁶ Polycrystalline thin films of YIG have been shown to exhibit a gradual increase in real permeability with frequency as opposed to a decrease observed in bulk ferrite toroids of the same composition. The films appear to be useful in the construction of rf microstructures.⁸⁷

The demand for soft ferrites has been growing and ferrites will expand markedly in both quantity and the extent of application as the need for ferrites of higher quality increases. The electromagnetic properties of ferrites depend on the production process and micro and nanostructures. MnZn ferrite is a principal ferrite for high permeability and power uses. Spray roasting method of Mn-Zn-Fe ternary system has been developed recently.⁸⁸ Precise control of production process to avoid the defects is the key to achieve high performance ferrites. New applications of ferrites such as ferrite carriers and toners for electrophotocopy and biochemical applications is expanding.

Noise filter characteristics of a common-mode choke coil fabricated from a nanocrystalline Fe₈₄Nb₇B₉ alloy were studied with the aim of clarifying its potential for application as a core material.⁸⁹ The impulse attenuation characteristics of the choke coil with the nanocrystalline alloy core are superior to those of one with an Mn-Zn ferrite core. The choke coils made from the nanocrystalline alloy and the amorphous alloy cores showed

higher attenuation in the frequency f range > 1 MHz. The common-mode attenuation of the choke coil with the nanocrystalline alloy core exhibited attenuation values higher than those of the ones with the other two cores in the frequency f range > 4 MHz. The conducted radio noise characteristics of the choke coil with the nanocrystalline alloy core are superior to those of the one with the amorphous alloy core. The attenuation of the former was 5 dB higher than that of the latter.

5.6 Nanocomposite Magnets

The recently developed nanocomposite magnets are composed of magnetically soft and hard ultra-fine grains whose magnetization are coupled by the intergrain exchange interaction. Because of the presence of soft grains and the coupling of the magnetization, nanocomposite magnets are expected to have superior hard magnetic properties such as high remanence, large energy product, and small temperature coefficient of the remanence as well as high coercivity.⁹⁰ A recent surge in the research interest in this field showed that the nitride of the rare earth-iron compound to exhibit good magnetic properties. Also, the application of mechanical alloying technique for the synthesis of the rare earth-iron compound is more versatile.⁹¹

5.7 Magnetic Refrigerant

Upon the application of an external magnetic field, the magnetic spins in a material partially align with the field, thereby reducing the magnetic entropy of the spin system. When performed adiabatically, the specimen's temperature will rise. This temperature rise related to the entropy change by the heat capacity, is known as the magnetocaloric effect. Upon cycling the magnetic field, this effect can be used for transferring heat from one thermal reservoir to another, forming the basis for a magnetic refrigerator. Composite magnetic materials containing nanometer-size magnetic species could possess enhanced magnetocaloric effects especially at high temperatures or low magnetic fields over a large temperature range.⁹² Enhanced magnetocaloric effect has been reported for a series of iron substituted gadolinium garnets (GGIG) $\text{Gd}_3\text{Ga}_{5-x}\text{Fe}_x\text{O}_{12}$, which was consistent with superparamagnetic behavior at low Fe concentrations and in qualitative agreement with calculation.⁹³

5.8 High- T_c Superconductor

Due to their small coherence lengths, the high T_c cuprates can be used as superconducting interconnects with widths of a few tens of nanometers, or as Josephson junctions with a surface area of a few hundred square nanometers. Therefore nanopatterning of these materials has become an attractive research undertaking.⁹⁴

5.9 Ferrofluids

Applications of ferrofluids include lubrication, sealing, air-moisture absorption, medical application and electrically conducting fluids for electromechanical systems.⁹⁵ Ferrofluid seals, ferrofluids sustained by a magnetic field in the desired position, has the advantages of both contact and hydrodynamic seals. They have low friction moment and

high degree of sealing, and can be used to seal vacuum systems and high pressure chambers, and separate different media. Ferrofluid lubricants can be easily positioned by a magnetic field to the exact friction zone, which may be difficult for traditional lubricants to fulfill. Ferrofluids can also find applications for damping oscillations and as a shock absorber. Shock absorbers made with ferrofluids have high supporting power and good amplitude-frequency characteristics.

The use of ferrofluid for cooling devices where magnetic fields are present is particularly promising. The possibility of intensifying convection at the expense of a magnetic field converts a magnetic fluid into a highly effective heat carrier. In addition it can be used as a tool to control heat transfer.

Ferrofluid based devices include sensors and actuators. For example, ferrofluids have been used in densimeters, accelerometers, pressure transducers, displacement transducers and slope angle-data transmitters. Applying a magnetic field to a ferrofluid, it is possible not only to position it easily, but to displace it easily or to change its shape. The basic advantages of such a mechanism lies in the absence of movable mechanical parts and, hence, in improved reliability. Typical examples of an actuator using ferrofluids are electromechanical converters, electrical contacts, displays, and level detectors.

Since a magnetic fluid is either black or brown, it may be used as inks in a printer controlled by a magnetic field. In spite of their relatively slower printing speed, advanced design may make it possible to print at higher speeds.⁹⁶ They can also be used as magnetic toner in xerography.

Methods to prepare nanometer-sized $\gamma\text{-Fe}_2\text{O}_3$, Fe, other transition metal or rare earth magnetic particles coated with carbon or organic layers have been reported.⁹⁷⁻⁹⁹ The coated magnetic particles are described to extend the applications in stabilizing ferrofluids and as contrast agent in magnetic resonance imaging.

5.10 Biological Applications

Ferritin is a natural constituent of the metabolic system in most animals. It consists of a segmented protein shell and inner space filled with a hydrated iron oxide similar to ferrihydrite. It provides one of the ways for the organism to store Fe^{3+} for physiological needs. It has been recently shown that, following removal of the ferrihydrite core, it is possible to reconstitute the empty protein shell under controlled oxidative conditions, tailored to the synthesis of magnetite rather than ferrihydrite.¹⁰⁰ In addition to the potential for the production of novel nanophase materials derived from biological materials, nanoscaled magnets are also potentially useful in magnetic resonance imaging and controlled drug delivery as a biocompatible ferrofluid. The synthesis and understanding of artificial (and natural) ferritin proteins has been advancing rapidly. New technology in molecular chemistry are now realizing the possibility of creating true molecular magnets, in which the magnetic ions are added one at a time and the resulting magnet has precisely defined atomic weight and magnetic properties, for example being able to target at specific tissues.¹⁰¹

Another case of interest and importance is magnetotactic bacteria. There is evidence for a magnetic direction finding ability in many species and this suggests some

interesting biomimicking possibilities in relation to both the magnetic sensors and the transducers. Currently our understanding in this area is limited to a group known as magnetotactic bacteria, which use the earth's magnetic field to enable themselves to orientate and move in the direction of nutritional or chemical gradients.¹⁰² The permanent magnetic dipole moment of each magnetotactic cell is due to intracellular membrane bounded single domain inorganic particles, which are arranged in chains. Most of the particles, known as magnetosomes, contain magnetite Fe_3O_4 , or greigite Fe_3S_4 in the 40 nm to 100 nm size range.¹⁰³

Methods for the large-scale preparation of biodegradable and biocompatible magnetic nanospheres has been developed.¹⁰⁴ The nanospheres can be used for cell labeling in magnetic cell separation techniques. The nanospheres proved to be immunospecific, biodegradable, and biocompatible. These immunospecific magnetic nanospheres are expected to have a large number of applications as biopharmaceutical reagents in biology and medicine.

6. FUTURE RESEARCH OPPORTUNITIES

The development of more sophisticated nanophase magnetic materials with engineered physical properties will lead to substantial improvements in the quality of materials for future Defense applications. There is great potential to employ nanophase materials in the development of superior smart materials (non-observables, *etc.*), non-volatile data recording media, communications equipment, sensors, and medical applications.

From a review of the rapid progress of synthesis and property manipulation of nanophase magnetic materials, several promising research opportunities come to mind. The suggested focus of future research initiatives related to the study of nanophase magnetic materials include the following:

- The investigation of the effects of shape, size, and composition on the magnetic properties of nanoparticles in composites, fluids, and gels.
- Synthesis of nanophase materials, for example self assembly processes in confined media including reverse micelles, microporous solids, Fullerenes, and other structured media.
- Synthesis nanocomposite magnets with optimum remanence and coercivity, improving design and optimization of compact and ultralight magnets for microwave/millimeter-wave application, electron beam focusing, cross-field amplifier, and telescopes.
- Novel synthesis of nanocrystalline and nanocomposite magnetic materials, for example, using pulsed-laser-deposition.

- Preparation and characterization of Terfenol-D with emphasis on their applications in micro-actuators, micro-positioning systems, missile guiding devices and in micro-switching and triggering devices. Thin film form of Terfenol-D included.
- Synthesis of metallic/insulating nanocomposite magnets with low Eddy current loss for devices operating at high frequencies.
- Design of new nanophase composites that will influence the exchange between nanograins and affect the magnetic behavior.
- Mechanisms to disperse nanograins on surfaces or in composites to produce uniform organized arrays
- Theoretical predictions of nanophase properties, especially structure - property relationships, that may be used to predict coercivities and superparamagnetism.
- Understanding the exchange coupling mechanism between single domain particles (often superparamagnetic), and between hard and soft magnets.
- Ultrahigh density magnetic recording media and advanced writing/reading characteristics.
- Study of nanophase Co/EuS macroscopic ferrimagnets for the understanding of their magnetic coupling and for application in high density magneto-optical recording media. which has shown promise of large signal-to-noise ratio at short wavelengths.
- Improving electromagnetic wave absorbing capability at high frequencies of ferrite nanocomposite coatings by structural alteration. And study of amorphous /nanocrystalline magnetic materials used as noise filter and shielding.
- Tribological study of nanocomposite/nanolayered magnetic films of various kinds. Incorporation, or elimination, of protective coating and magnetic media by combining desirable mechanical and magnetic properties.

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7. REFERENCES

1. Yamamoto, T., Shull, R.D., Bandaru, P.R., Cosandey, F., Hahn, H.W., *Jpn. J. Appl. Phys.*, Part 2, 33(9B), L1301-1303, **1994**.
2. Yamamoto, T., Tsukui, S., Funtai K. K., 33(3), 170-5, **1996**.
3. Cao, M., Deng, Q., Wuji H. X., 12(1), 88-91, **1996**.
4. El-Shall, M.S., Li, S., Graiver, D., Pernisz, U., *ACS Symp. Ser.* 622, (*Nanotechnology*), 79-99, **1996**; and references therein.
5. Klabunde, K.J. et al, *NATO ASI Ser. E*, 260(*Nanophase Materials*), Hadjipanayis, G.C., and Siegel, R. W. Eds., 1-19, **1994**; and references therein.
6. Hadjipanayis, G.C., Tang, Z.X., Gangopadhyay, S., Yiping L., Sorensen, C.M., Klabunde, K.J., Kostokas, A., and Papaefthymiou, V., *Studies of Magnetic Properties of Fine Particles and their Relevance to Magnetic Science*, Dormann, J.L. and Fiorani, D., Eds., 35-46, **1992**.
7. Bi, X.X., Ganguly, B., Huffman, G.P., Huggins, F.E., Endo, M., Eklund, P.C., *J. Mater. Res.*, 8(7), 1666-74, **1993**.
8. Zhao, X.Q., Liang, Y., Zheng, F., Hu, Z.Q., Zhang, G.B., Bai, K.C., *Mater. Res Soc. Symp. Proc.*, 368, 39-43, **1995**.
9. Rozman, M., and Drofenik, M., *J. Am. Ceram. Soc.*, 78(9), 2449-55, **1995**.
10. Hadjipanayis, G.C., Tang, Z.X., Gangopadhyay, S., Yiping L., Sorensen, C.M., Klabunde, K.J., Kostokas, A., and Papaefthymiou, V., in "*Magnetic Properties of Fine Particles*," Editors: Dormann J.L. and Fiorani, D., Elsevier Science Publishers, 35-45, **1992**.
11. Lee, C.K., Speyer, R.F., Spratt, G.W.D., *J. Appl. Phys.* 73(10), 6266-6268, **1993**.
12. Sankaranarayanan, V. K., Khan, D. C., *J. Magn. Magn. Mater.*, 153(3), 337-46, **1996**.
13. Yogo, T., Nakamura, T., Kikuta, K., Sakamoto, W., Hirano, S., , *J. Mater. Res.*, 11(2), 475-82, **1996**.
14. Pramanik, P.; *Bull. Mater. Sci.*, 18(6), 819-29, **1995**.
15. Eppley, H.J., Wang, S., Tsai, H.-L., Aubin, S.M., Folting, K., Streib, W.E., Hendrickson, D.N., Christou, G., *Mol Cryst Liq Sci Technol Sect A.*, 274, 815-22.
16. Eppley, H.J., Tsai, H.-L., de Vries, N., Folting, K., Christou, G., Hendrickson, D.N., *J Am Chem Soc*, 117(1), 301-17, **1995**.
17. Pillai, V.; Kumar, P.; Hou, M. J.; Ayyub, P.; Shah, D. O., *Adv. Colloid Interface Sci.* 55, 241-69, **1995**, and references therein.
18. Moumen, N., Pileni, M. P., *Chem. Mater.*, 8(5), 1128-34, **1996**
19. Kommareddi, N.S., Tata, M., John, V.T., McPherson, G.L., Herman, M.F.; Lee, Y.-S., O'Connor, C.J.; *Chem. Mater.*, 8(3), 801-9, **1996**
20. Tanori, J.; Duxin, N., Petit, C.; Lisiecki, I., Veillet, P., Pileni, M. P., *Colloid Polym. Sci.*, 273(9), 886-92, **1995**.
21. Lado-Tourino, I. Gonzalez-Penedo, A. Lopez-Quintela, M. A., Garcia-Otero, J., Garcia-Bastida, A. J., Izco, C., Baldomir, D., Sanchez, R. D., Rivas, J., Greneche, J. M., *Nanostruct. Non-Cryst. Mater., Proc. Int. Workshop Non-Cryst. Solids*, 4th , **1995**.

22. Bhabra, V., Lal, M., Maitra, A. N., Ayyub, P., *J. Mater. Res.*, 10(11), 2689-92, **1995**.
23. Krätchmer, W., Fostiropoulos, K., Huffman, D. R. *Chem. Phys. Lett.* 170, 167, **1990**.
24. Iijima, S. *Nature*, 354, 56-58, **1991**.
25. Guerrer-Piécourt, C., Le Bouar, Y., Loiseau, A., Pascard, H. *Nature*, 372, 761-765, **1994**.
26. Terrones *et al.*, *Proc. Electrochem. Soc.*, 95-10, 599-620, **1995**.
27. Brunsmen, E. M., Anna, S., Majetic, S. A., McHenry, M. E. *Mater. Res. Soc. Symp. Proc.*, 359, 35-40, **1995**.
28. Majetic, S. A., Scott, J. H., Brunsmen, E. M., Kirkpatrick, S., McHenry, M. E., Winkler, D. C., *Proc. Electrochem. Soc.*, 95-10, 584-598, **1995**.
29. Grushko, Y. S., Kolesnik, S. G., Pershikova, T. M., Sovestnov, A. E., Voronin, V. V. Materov, V. F., Sobolevskii, V. K. *Proc. Electrochem. Soc.*, 95-10, 648-653, **1995**.
30. Tsang, S.C., Chem, Y.K., Harris, P.J.F., Green, M.L.H. *Nature*, 372, 159-162, **1994**.
31. Ajayan, P. M., Iijima, S., *Nature*, 361, 333-334, **1993**
32. Ajayan, P.M., *et al.*, *Nature*, 362, 333-334, **1993**.
33. Ajayan, P.M., Stephan, O., Redlich, P., Colliex, C., *Nature*, 375, 564-567, **1995**.
34. Parvin, K., Weathersby, S.P., Awadallah, S., LaDuca, R., Ruoff, R.S., Subramoney, S., Van Kavelaar, P., Nolan, P.E., Jiao, J., *Proc. Electrochem. Soc.*, 95-10, 570-83, **1995**.
35. Ziolo, R.F., Giannelis, E.P., Weistein, B.A., O'Horo, M.P., Ganguly, B.N., Mehrotra, V. Russell, M.W., Huffman, D.R., *Science*, 257, 219-223, **1992**.
36. Giannelis, E.P., Mehrotra, V., Vassiliou, J.K., Shull, R.D., MacMichael, R.D. and Ziolo, R.F., *NATO ASI Ser. E* , 260(*Nanophase Materials*), Hadjipanayis, G.C., and Siegel, R. W. Eds., 617-623, **1994**.
37. Bein, T. In *Supramolecular Architecture in Two and Three Dimensions*; T. Bein, Ed., (American Chemical Society, Washington, D. C.) 499, 274-293, 1992 and the references therein.
38. Ziethen, H. M. *et al.*, *Catal. Today*, 8, 427-38, 1991.
39. Hussain, I. *et al.*, *Mater. Res. Soc. Symp. Proc.*, 384, 529-34, 1995.
40. Garcia, J. L., Lazaro, F. J., Martinez, C., Corma, A., *J. Magn. Magn. Mater.*, 140-144, 363-4, 1995.
41. Abe, T., Tachibana, Y., Uematsu, T., Iwamoto, M., *J. Chem.Soc.,Chem. Commun.*, 1617-18, **1995**.
42. Schunemann, V., Winkler, H., Ziethen, H.M., Schiller, A., and Trautwein, A.X., in *Studies of Magnetic Properties of Fine Particles and Their Relevance to Materials Science*, Editors, Dormann, J.L. and Fiorani, D., Elsevier Science Publishers, 371-380, **1992**.
43. Meldrum, F.C., Heywood, B.R., Mann, S., *Science*, 257(5069), 522-3, **1992**.
44. Pierre,T.G., Sipos, P., Chan, P., Chua-Anusorn, W., *NATO ASI Ser. E*, 260(*Nanophase Materials*), Hadjipanayis, G.C., and Siegel, R. W. Eds., 49-56, **1994**.
45. Schultz, L., Kuhrt, C., Schnitzke, K., Wecker, J., Katter, M., *Trans. Mater. Res. Soc. Jpn.*, 6A (*Computations, Glassy Materials, Microgravity and Non-Destructive Testing*), 63-8, **1994**.

46. Umemoto, M., Yien, J., Kakoo, S., Raviprasad, K., Okane, I., Hirose, S., *Funtai oyobi Funmatsu Yakin*, 42(1), 16-21, **1995**.
47. Cheung, C., Erb, U., *Novel Tech. Synth. Process. Adv. Mater. Proc. Symp.*, Singh, Jogender; Copley, Stephen M., Eds., (Minerals, Metals & Materials Society Publishers, Warrendale, Pa.), 455-63, **1994**.
48. Erb, U., *Can. Metall. Q.*, 34(3), 275-80, **1995**.
49. Cheung, C., Nolan, P., and Erb, U., *Mater. Lett.*, 20(3-4), 135-8, **1994**.
50. Cheung, C., Nolan, P., and Erb, U., *Scr. Metall. Mater.*, 31(6) 735-40, **1994**.
51. Gleiter, H.; *Mater. Sci. Forum*, 189/190, 67, **1995**.
52. Leslilie-Pelecky, d.L. and Rieke, R.D., *Chem Mater*, 8, 1770, **1996**.
53. Awschalom, D. P. DiVincenzo and J. F. Smyth, *Science*, 258, 414, **1992**.
54. Zhang, J. M. Hernandez, J. Tejada and R. F. Ziolo, *Phys. Rev. B* 54, **1996**.
55. Zhang, R. Ziolo, E. C. Kroll, X. Bohigas and J. Tejada, *J. Magn. Magn. Mater.*, 140/144, 1853, **1995**.
56. Friedman, M. P. Sarachik, J. Tejada and R. Ziolo, *Phys. Rev. Lett.*, 76, 3830, **1996**.
57. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, *Science*, 265, 1054, **1994**.
58. Shull, U. Atzmony, A. J. Shapiro, L. J. Swartzendruber, L. H. Bennett, W. J. Green and K. Moorjani, *J. Appl. Phys.*, 63, 4261, **1988**.
59. Yamamoto, R. D. Shull, P. R. Bandaru, F. Cosandey and H. W. Hahn, *Jpn. J. Appl. Phys.*, 33, L1301, **1994**.
60. Yamamoto, R. D. Shull, and H. W. Hahn, *Proc. 3rd Intern. Conf. Nanostructured Mater.*, 1996 in press.
61. Yoshizawa, Y., Mori, H., Arakawa, S., Yamauchi, K., *Nippon Oyo Jiki Gakkaishi* 19 457, **1995**.
62. Bodker, F., Morup, S., *Nucl. Instrum. Methods Phys. Res., Sect. B* 108, 413, **1996**.
63. Frenkel, J. and Dorfman, J., *Nature*, 126, 274, **1930**.
64. Stoner, E.C. and Wohlfarth, E.P., *Proc Phys Soc A*, 240, 599, **1948**.
65. Holz, A. and Scherer, C., *Phys Rev B*, 50, 6209, **1994**.
66. Zhu, J., Ye, X., *Trans. Mater. Res. Soc. Jpn.* 15B, 881, **1994**.
67. Chui, S.T., Tian, D.C., *J. Appl. Phys.*, 78, 3965, **1995**.
68. Sellmyer, D.J., *Nanophase Materials*, Hadjipanayis, G.C., Siegel R.W., Eds., (Kluwer Academic Publishers, Netherlands, 537, **1994**.
69. Wang, Y.J., *J. Magn. Soc. Jpn.*, 17, Suppl. S1, 294, **1993**.
70. Sellmyer, D.J., Kirby, R.D., Chen, J., Wierman, K.W., Shen, J.X., Liu, Y., Robertson, B.W., Jaswal, S.S., *J. Phys. Chem. Solids* 56, 1549, **1995**.
71. Brown, J., *Sensors*, 42, **September 1994**.
72. Moodera, L. R. Kinder, T. M. Wong and R. Meservey, *Phys. Rev. Lett.*, 74, 3273, **1995**.
73. Miyazaki and N. Tezuka, *J. Magn. Magn. Mater.*, 139, L231, **1995**.
74. Fujimori and S. Mitani, *J. Appl. Phys.*, 79, 4733, **1996**.
75. Yogi, T. A. Nguyen, *IEEE Trans. Mag.* 29, 307, **1993**.
76. S. Murdock, R. Simmons, R. Davidson, *IEEE Trans. Mag.* 28, 3078, **1992**.
77. Ch. Tsang, *Proc. IEEE* 81 (9), 1344, **1993** and references therein.
78. R. Coffey, M.A. Parker, J. K. Howard, *IEEE Trans. Mag.* 31, 2737, **1995**.
79. Farrow, D. Weller, R.F. Marks, M.F. Toney, A. Cebollada, G.R. Harp, *J. Appl. Phys.*

- 79, 5967, 1996.
80. David Lambeth, presented at *40th Magnetism and Magnetic Materials Conference*, Philadelphia, USA, Nov. 6-9, 1995.
81. Chou, P.R. Krauss, Linshan Kong, *J. Appl. Phys.* 79, 6101, 1996.
82. Chou, P.R. Krauss, *J. Appl. Phys.* 79, 5066, 1996.
83. Maya, L., Thundat, T., Thompson, J.R., Stevenson, R.J., *Appl. Phys. Lett.*, 67, 3034, 1995.
84. Daughton, J.M., *Thin Solid Films*, 216, 162, 1992.
85. Huiberts, J.N.; Griessen, R.; Rector, J.H.; Wijngaarden, R.J.; Dekker, J.P.; de Groot, D.G.; Koeman, N.J; *Nature*, 380, 231, 1996.
86. Bush, *J Appl. Phys.*, 73, 6307, 1993.
87. Bush, *J. Appl. Phys.*, 73, 6310, 1993.
88. Yoshimatsu, H and Narutani, T; *Jpn. Patent*, 83819, 1991.
89. Kimura, Y.; Makino, A.; Inoue, A.; Masumoto, T; *Nippon Oyo Jiki Gakkaishi* 18, 805, 1994.
90. Fukunaga, H., *Nippon Oyo Jiki Gakkaishi* 19, 791, 1995.
91. Umemoto, M; Yien, J; Kakoo, S; Raviprasad, K.; Okane, I; Hirose, S; Funtai O; Funmatsu Y; 42, 16, 1995.
92. Shull, R.D., McMichael, R.D., Ritter, J.J., Bennett, L.H., *Mater. Res. Soc. Symp. Proc.* 286, 449, 1993.
93. McMichael, J.J. Ritter and R. D. Shull. *J. Appl. Phys.*, 73, 6946, 1993.
94. Mannhart, J; *Phil. Trans. R. Soc. Lond. A* 353, 377, 1995.
95. Berkovsky, B.M., Medvedev, V.F., Krakov, M.S., *Magnetic Fluids, Engineering Applications*, (Oxford University Press, New York) 1, 1993.
96. Maruno, S., Yubakami, K., Soga, N., *J. Magn. Magn. Mater.*, 39, 187, 1987.
97. Liu, Q., Xu, Z., *J. Appl. Phys.* 79, 4702, 1996.
98. McHenry, M.E., Majetich, S.A., Kirkpatrick, E.M., *Mater. Sci. Eng.*, A 204, 19, 1995.
99. Nuhfer, N.T., DeGraef, M., McHenry, M.E., Majetich, S.A., Artman, J.O., Staley, S.W., *Electron Microsc. Proc. Int. Congr. Electron Microsc.*, 13th, Jouffrey, B., Colliex, C., Eds., (Editions de Physique, Les Ulis, Fr., 1994), 2A, 313, 1994.
100. Meldrum, F.C., Heywood, B.R., Mann, S., *Science* 257, 522, 1992.
101. Gatteschi, D., Caneschi, A., Pardi, L., Sessoli, R., *Science* 265, 1054, 1994.
102. Dickson, D.P.E., *Nanophase Materials*, Hadjipanayis, G.C., Siegel R.W., Eds., (Kluwer Academic Publishers, Netherlands), 729, 1994.
103. Frankel, R. B., Blakemore, R.P., *Bioelectromagnetics* 10, 223, 1989.
104. Winoto-Morbach, S., Mueller-Ruchholtz, W., *Eur. J. Pharm. Biopharm.*, 41, 55, 1995.